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A STUDY OF BONDING BETWEEN GLASS AND PLASTIC  
IN GLASS-REINFORCED PLASTICS; PHASE I

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## I INTRODUCTION

This report covers the second quarter of work on a study of "bonding" between glass and plastic in glass-reinforced plastics. Current practice in the preparation of glass-reinforced plastics includes treatment of the glass fibers (or fabric) with a "finish" to insure adhesion or "bonding" of the subsequently applied plastic. Such "bonding" as may result is supposedly due to the formation of an Si-O-A linkage between the glass surface (SiO) and the finishing agent (A), where A may be Si (as in commercial silane finishes) or Cr (as in certain other commercial finishes). This study concerns other types of "bonding" between organic phase and glass phase which do not rely upon the hydrolytically reactive Si-O-A linkage.

## II OBJECTIVE

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The objective of Phase I of this project is to investigate methods for halogenation of a glass surface, with formation of silicon-chlorine or silicon-fluorine bonds.

## III SUMMARY

Ottawa sand, sea sand (Merck), and Eccospheres S-1 have been chlorinated with phosgene to give products containing up to 51 micrograms of chlorine per gram of silica. The concentration of chlorine has been studied as a function of temperature from 425°C to 1025°C. Optimum temperature for reaction is about 450°C.

Based on conditions of reaction and of post-reaction handling, as well as comparison of the above data with the results of blank and control samples of quartz we are lead to believe that chlorine is probably not present as physically adsorbed atoms or molecules, and that a Si-Cl bond has been formed.

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## IV EXPERIMENTAL

### Materials

Ottawa sand, sea sand (Merck), and Eccospheres S-1 (a commercial, high purity, amorphous silica which was crushed and screened to 80 mesh and finer) were used in this work. The surface area of these samples was determined by the method of Nelson and Eggertsen.<sup>1</sup> This method involves adsorption of nitrogen from a flowing mixture of nitrogen and helium. The values found were: Ottawa sand, 0.06 square meters per gram; sea sand, 0.08; and crushed Eccospheres S-1, 0.24.

Phosgene was used almost exclusively for chlorination of silica. A mixture of chlorine and finely divided carbon was also effective, but an impractical length of time was required for the larger particles of carbon to react. If these were not removed by reaction they remained as an undesirable, inseparable contaminant in the final product. Therefore work with carbon was discontinued when it was found that phosgene was effective.

### Apparatus

A fluidized bed reactor, described in Quarterly Report No. I, was used for initial work up to about 600°C. At higher temperatures, this reactor collapsed, apparently at the ring seal which supported sintered quartz disc.

A new reactor design for carrying out these reactions is shown in Fig. 1. The apparatus was mounted on the arm of a shaker apparatus. Shaking for a very short period resulted in a slow, but thorough, circulation of the finely divided charge of silica. The reactant chamber was heated with a heating tape for some of the low temperature runs, with a gas-air flame for the other low and the intermediate temperature runs, and with a gas-oxygen flame for high temperature (800-1000°C) runs.

Temperature in the circulating bed was measured with a Chromel-Alumel thermocouple and a Leeds and Northrup potentiometer. Reactant gas (phosgene) was measured with a Fischer-Porter sapphire-ball flow meter, and admitted through a Tygon, or natural rubber tubing connection. Exit gases were vented to a dry ice-cooled trap, and thence to a fume hood.

The only difficulty in the operation of this reactor was the non-uniform temperature distribution through the sample at high temperatures. This difficulty has not yet been resolved, but at present there is no urgent need to do so.

#### Experimental Procedure

A weighed quantity of silica (5 to 30 g) was placed in the quartz reactor, the reactor mounted on the shaker arm, and the reactant inlet and vent tubes connected. As commercial high purity nitrogen (99.99%, dew point -85°C.) was slowly flushed through the apparatus, the sample was raised to the desired reaction temperature. These conditions were maintained for one hour, to remove volatile impurities, and the nitrogen was replaced by phosgene, at a flow rate of 15 ml per minute.

The temperature and flow rate of phosgene were maintained for 2 to 4 hours, the phosgene was replaced by nitrogen, and the reaction product was flushed, at the temperature of the reaction, for one-half hour. Heating was discontinued and the product allowed to cool under the flowing stream of nitrogen. The product was then given a post-reaction treatment in a vacuum oven at 110°, at a pressure less than 5 mm Hg, and for at least 16 hours. This post-reaction treatment was intended to remove chlorine that was physically adsorbed.

#### Analytical

Chlorinated silica samples were analyzed by leaching a weighed sample (2-5 g) with deionized water, and determining chloride concentration

Table I

## CHLORINATION OF SILICA WITH PHOSGENE

Notebook and page number	Temp. (°C)	Time (hrs)	µg Cl/gm Si		Post Reaction Evacuation at 100°C and < 5 mm Hg	Remarks
			Sample	Blank		
4965 - 13	830	4	2.04		overnight	Ottawa sand unless otherwise noted. Phosgene flow rate = 15 ml/min
4965 - 14	725	4	2.28		over weekend	
4965 - 17	625	4	13.50		overnight	Phosgene
4965 - 19	1020	2	0.91		15 hours	Flowrate = 15 ml/min. Much condensate in vent trap
4965 - 20	623	4	13.30		22 hours	
4965 - 21	725	4	3.29		67 hours	
4965 - 23	833	4	1.99		17 hours	
4965 - 25	1020	2	0.41		18 hours	Much condensate in vent trap
4965 - 26	R.T.	0		2.92	0 hours	Immediate analysis
4965 - 26	1030	2-1/2		0.42	0 hours	Exposed to air, in a stoppered bottle, for 23 hours
4965 - 26	1030	2-1/2		0.37	0 hours	Immediate analysis
4965 - 28	620	4-1/2		0.85	0 hours	
4965 - 29	525	4	18.27		19 hours	Very small amount of condensate in vent trap
4965 - 31	525	4	17.30		68 hours	
4965 - 33	425	4	20.92		18 hours	Very small amount of condensate
4965 - 35	525	4	0.52		18 hours	Flushed with N <sub>2</sub> at 1020°C for 2 hrs after chlorination
4965 - 37	525	4	2.57		18 hours	Flushed with N <sub>2</sub> at 800°C for 2 hrs after chlorination
4965 - 40	525	1	14.80		19 hours	Very little condensate in vent trap
4965 - 41	525	2	23.55		43 hours	
4965 - 42	525	4	36.6		64 hours	Eccospheres S-1, crushed. Considerable con- densate in vent trap
4965 - 45	525	2	51.0		19 hours	Merck sea sand
4965 - 47	825	2	1.93		20 hours	Merck sea sand
4965 - 49	525	2	21.80		115 hours	Ottawa sand

on an aliquot of the solution with a micro-coulometric cell using a silver metal anode. The values reported as micrograms of chlorine per gram of silica are corrected for the traces of chloride found in the deionized water. Blank determinations were also run on untreated (control) samples of the materials. Analytical results are shown in Table I.

#### Reactions of Chlorinated Silica

A sample of chlorinated Ottawa sand (21.8  $\mu\text{g Cl/g sand}$ ) was treated with 1-naphthylmagnesium bromide. At the same time, a sample of the non-chlorinated sand was treated with the Grignard reagent in the same manner, as a control. The two samples were washed thoroughly to remove all soluble organic materials. They were then dried at 1-2 mm Hg, and ambient temperature, to sublime away adsorbed naphthalene.

The fluorescence of the experimental sample was greater visibly, than the control sample, when illuminated with light of 3660 or 2537 microns. The relative fluorescence of the experimental sample (as measured on an Aminco-Bowman spectrofluorometer), of the control, and of a blank (no treatment) are shown in Table II.

Table II  
Fluorescence of Naphthalene-Modified Quartz

Material	Exciting Wave Length (m $\mu$ )	Fluorescence Wave Length (m $\mu$ )	Relative Fluorescence
Chlorinated Ottawa sand, treated with 1-naphthylmagnesium bromide	390	550	42
	390	525	57
	210	550	67
	210	525	78
Control	390	550	10
	390	525	12
	210	550	26
	210	525	27
Blank	390	550	4
	390	525	5
	210	550	18
	210	525	18

## V DISCUSSION

The chlorination of silica with phosgene appears to be strongly affected by temperature, as shown by Table I, with a maximum value of 23.6 micrograms of chlorine per gram of Ottawa sand at 525°C. This value drops consistently, and fairly reproducibly, with increasing temperature, the highest temperatures (1020-1030°C), giving the lowest values (0.4-1.0 µg Cl/g sand).

That the background (or residual chloride) found on the sand does not contribute appreciably to the observed chloride content is shown by the four runs from notebook pages 26-28. Here, also, the amount of chloride was found to be least at the highest temperature, indicating that the very high temperatures result in "stripping" residual chloride from the sample.

This conclusion is supported by the two runs from pages 35 and 37. The chlorination reaction was run at 525°C, which should have resulted in a chlorine content of 15-25 µg Cl/g sand. Following this reaction, however, the samples were purged with nitrogen for two hours at 1020 and 800°C respectively. This treatment reduced the chlorine content to essentially that of any other samples run at those temperatures. The amount of white, chlorine-containing condensate in the vent trap was also observed to be greatest at 800-1000°C and least at 400-500°C.

The post-reaction treatment at low pressure and 110°C for several hours was adequate to completely desorb any chlorine, phosgene, HCl, etc., which may have been physically adsorbed on the surface. Therefore, it is a reasonable conclusion that the chlorine found on the samples is attached through a chemical bonding, or, at least, a chemisorption process.

Using the data from Table I, p 29, of 18.3  $\mu\text{g}$  Cl per gram of sand one may calculate the "population" of chlorine per unit surface area. 18.3  $\mu\text{g}$  of chlorine (atomic weight 35.46) is about 0.5 microgram atoms of chlorine, or,  $0.5 \times 10^{-6} \times 6.0 \times 10^{23}$  atoms of chlorine. These are distributed over an area of 0.06 square meters, (as found for Ottawa sand). Since one meter is  $10^{10}$  Angstrom units ( $\text{\AA}$ ), the Cl population is:

$$\frac{0.5 \times 10^{-6} \text{ micrograms-atoms Cl} \times 6.0 \times 10^{23} \text{ atoms/gram-atom}}{0.06 \text{ meters}^2 \times (10^{10} \text{ \AA/meter})^2}$$

$$= \frac{5 \times 10^{-7} \times 6 \times 10^{23}}{6 \times 10^{-2} \times 10^{20}}$$

= 5 atoms of chlorine per 100 square Angstroms.


For comparison, the van der Waal's radius of the chlorine atom is  $1.8 \text{ \AA}^3$ .

#### FUTURE WORK

Future work will place emphasis upon the anticipated reactions with fluorinating agents instead of chlorinating agents. Boron trifluoride will be used in initial fluorination experiments.

Proof of the state of combination of the halogen atoms bound to silica will also receive increased attention. To this end the use of very finely divided silica will permit, hopefully, identification of adsorbed vs chemisorbed molecules by infrared absorption measurements. In the case of fluorine, NMR (nuclear magnetic resonance) spectra may show the difference between a true Si-F bond and another fluoride ( $\text{BF}_3$ , HF, etc) adsorbed on  $\text{SiO}_2$ . The usefulness of NMR will depend upon the resolution one may obtain from molecules adsorbed on a solid of extremely fine particle size.

Respectfully submitted,

  
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3. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 1948, p. 187.

#### ACKNOWLEDGMENTS

Mr. Michael Bertolucci performed much of the work reported here. Dr. Harold Eding carried out the surface area determinations on the silica materials.

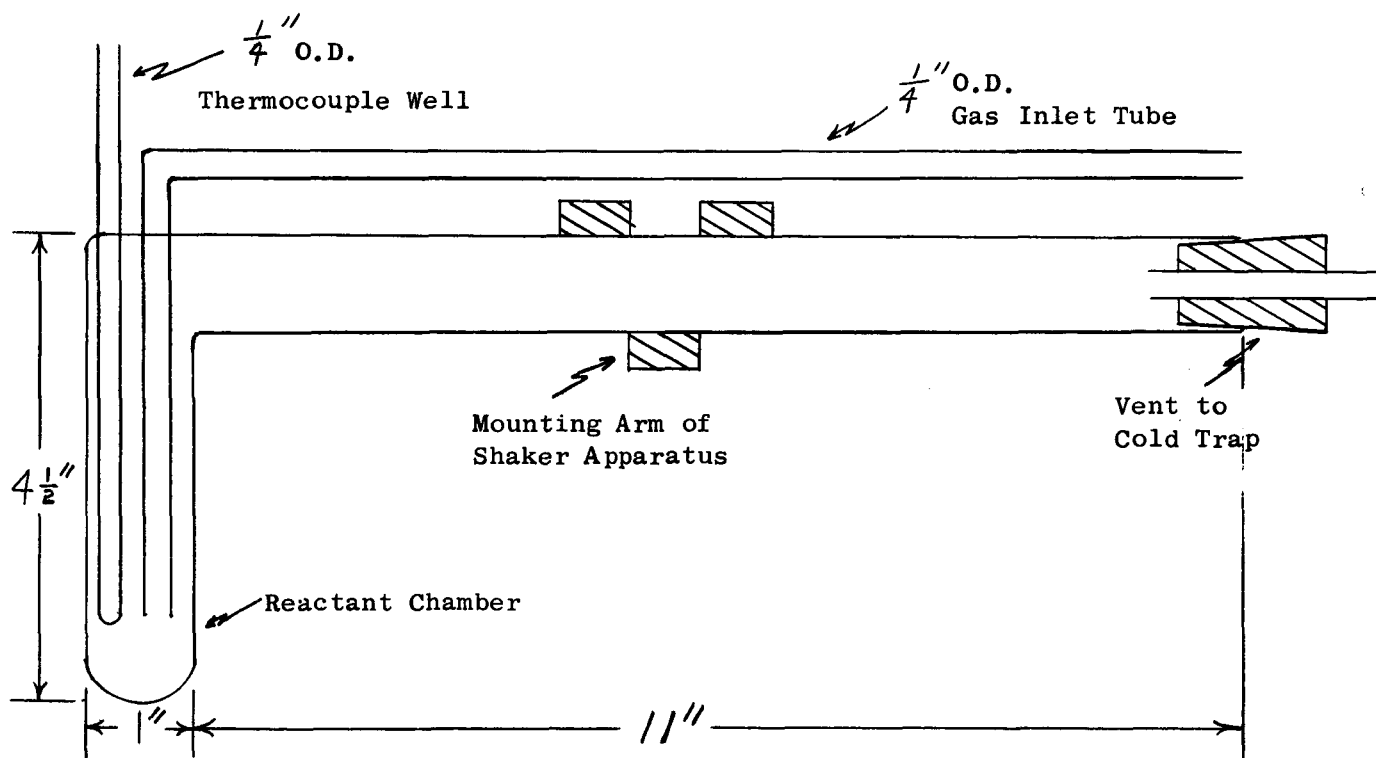


Fig. 1

Quartz Reactor for High Temperature  
 Halogenation of Silica